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Supporting Information

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High-Performance, Stretchable, Wire-Shaped Supercapacitors**

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Supporting Information

Experimental Section

Materials. Drawable vertically-aligned CNT arrays were grown on silicon wafer substrates with a layer of 400-nm thick silicon oxide coating by chemical vapor deposition according to previously reported procedures.[28-30] Poly(vinyl alcohol), PVA, (M_w =146,000-186,000, 99+% hydrolyzed) and Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate), PEDOT-PSS, (3.0-4.0% in H_2O, high-conductivity grade) were purchased from Sigma-Aldrich Corporation. Elastic wires (containing 64% polyester and 36% polyurenthane) were purchased from Gütermann Company, the outside thread was removed by hand prior to use.

Apparatus for characterization. Surface morphology of electrodes and devices were characterized using scanning electron microscopy (JEOL JSM-6510LV/LGS operated at 20 kV). Electrochemical measurements were performed on an electrochemical working station (CHI 760C, U.S.A.). To evaluate the stretchability of wire electrodes and devices, the electrical resistance of wire electrodes and electrochemical performance of wire-shaped supercapacitors were measured under stretching and bending by carefully fixing them onto a mechanical test machine (MV220 Motorized Test Stand, DS2-11 Digital Force Gauge; IMADA, Inc.) for stretching while the electrical and electrochemical properties were measured *in situ* .

Preparation of CNTs wrapped elastic electrodes. An elastic wire was fixed on two iron supports, which was stretched to different stains (30%, 60% and 100%). Then, CNT sheet was directly drawn from the drawable *as-grown* CNT array and carefully attached on the pre-strained wire. The CNT sheet was continuously wrapped around the pre-strained wire by rotating the wire back and forth by hand. Ethanol was dropped on the surface of the CNTs to make them compact and contact well with the elastic wire substrate. CNT-wrapped elastic wires with buckled surface structure were obtained after the pre-strain was released.

Fabrication of the stretchable wire-shaped supercapacitors. The resultant CNT- wrapped elastic wires were used as both active electrodes and current collectors. A polymer solution containing poly(vinyl alcohol) powder (10 g) and H_3PO_4 (10 g) in water (100 mL) was used as the gel electrolyte and separator in supercapacitors. The gel electrolyte was coated over the most part (70% length) of the CNT-wrapped elastic wires (3-4 cm long) and dried in the air at room temperature for about 4 hours. The wire-shaped supercapacitor was fabricated by carefully twisting two such electrolyte-coated CNT-wrapped wires together, followed by drop-coating electrolyte solution outside of the external surface of the assembled supercapacitor to ensure a good contact between electrodes and electrolyte. Finally, the end part of the CNT length free from the electrolyte coating was connected with a copper wire using silver paste for subsequent characterization of the device performance.

Evaluation of the electrochemical capacitance for supercapacitors. All of the electrochemical performance of supercapacitors were characterized based on two-electrode system unless stated otherwise. Cyclic voltammetry curves were obtained at the scan rate from 0.02 V s^{-1} to 0.1 V s^{-1}. Electrochemical impedance spectroscopy was carried out within a frequency range from 10^{-2} to 10^{5} Hz using a 5 mV AC voltage and a 0 V DC voltage. The specific capacitance for an entire cell of two-electrode system was calculated from the Equation 1,[34-37]

$$C_{cell} = \frac{I}{m\mathrm{d}V/\mathrm{d}t} \quad (1)$$

where, I is the applied discharge current, m is the mass of active materials at both electrodes, $\Delta V/\Delta t$ was calculated from the Equation 2, [34-37]

$$dV/dt = (V_2 - \frac{V_1}{2})/(T_2 - T_1) \qquad (2)$$

where, V_2 and V_1 are the potential after IR drop and the half potential of the discharge curve, respectively, T_2 and T_1 are the corresponding discharge time of V_2 and V_1. The specific capacitance for a single electrode (C_{single}) was calculated from the Equation 3, [34-37]

$$C_{single} = 4\, C_{cell} \qquad (3)$$

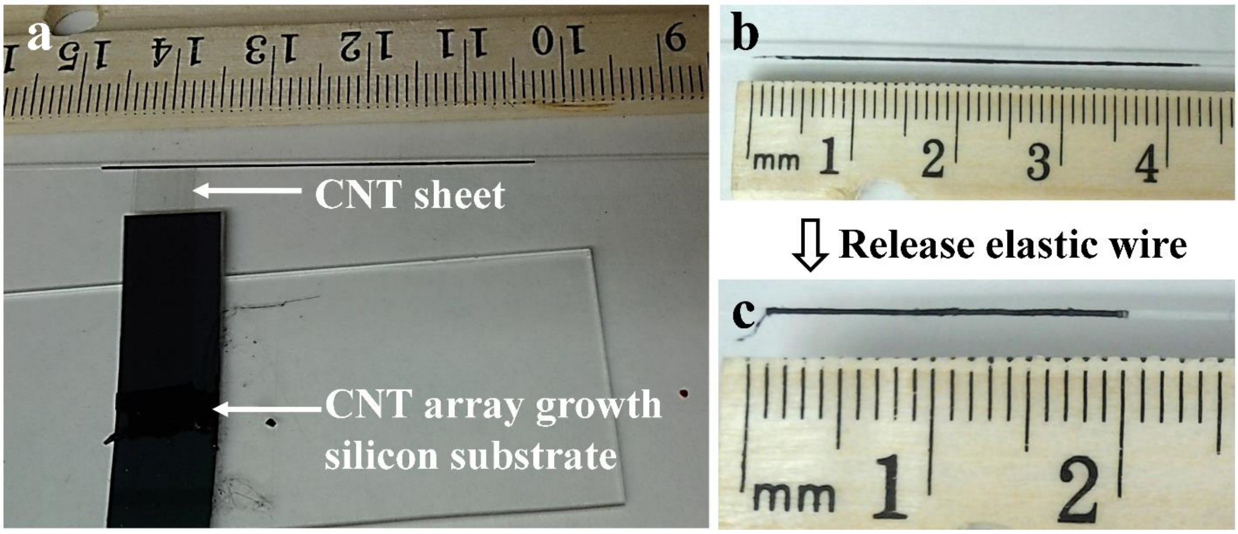

Figure S1. (a) The digital photograph of the process to wrap CNT sheet on a pre-strained elastic wire containing 64% polyester and 36% polyurenthane (Gütermann Company). (b,c) The CNT-wrapped elastic wire before (b) and after (c) releasing the tensile strain.

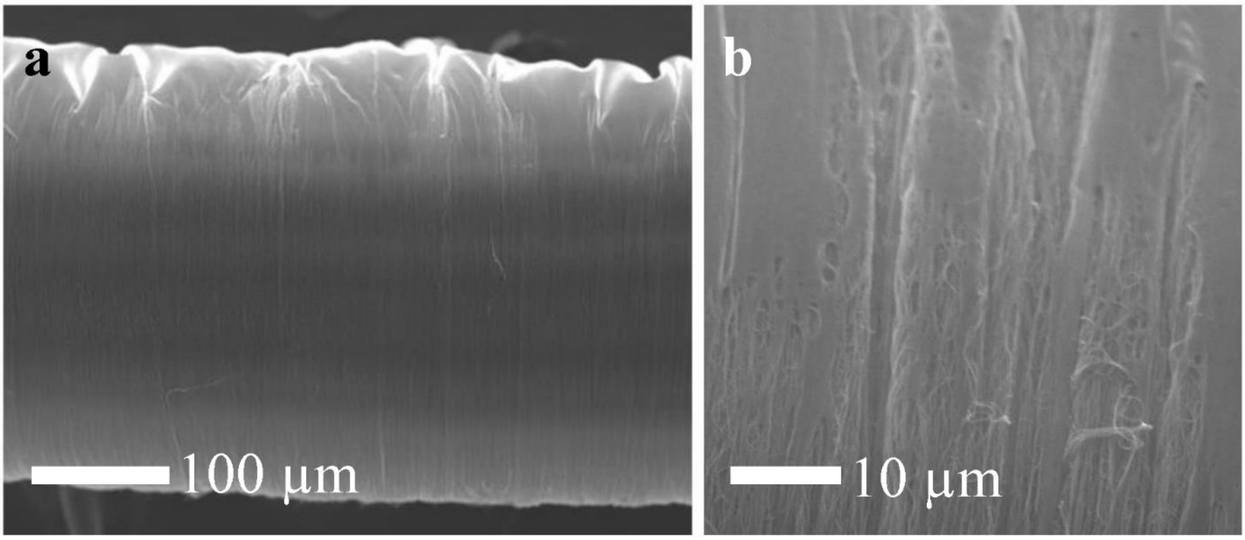

Figure S2. (a, b) SEM images of a CNT/PEDOT-PSS composite wire under different magnifications.

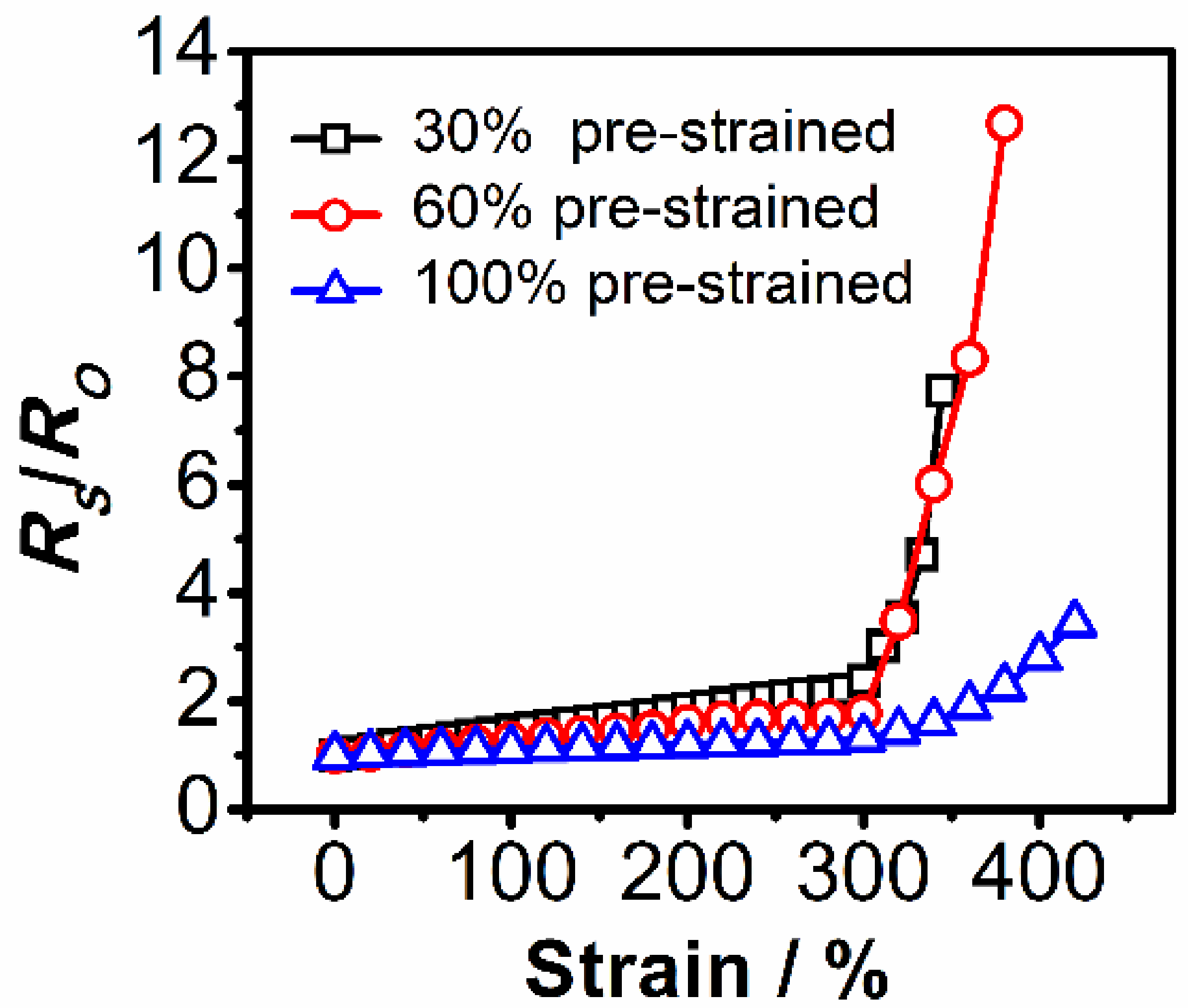

Figure S3. Change in electrical resistance as a function of tensile strain for the CNT-wrapped 64% polyester and 36% polyurenthane elastic wires coated with PVA (see text), R_S and R_O are the resistance before and after stretching. To investigate the dependence of electrical resistance on the tensile strain, we coated the CNT-wrapped elastic wire with a thin (~10 µm) layer of polyvinyl alcohol (PVA) to prevent possible CNT slipping from the surface of the elastic wire. The PVA-coated and CNT-wrapped elastic wire was then carefully fixed on a micro tensile test machine (MV220 Motorized Test Stand, DS2-11 Digital Force Gauge; IMADA, Inc.).

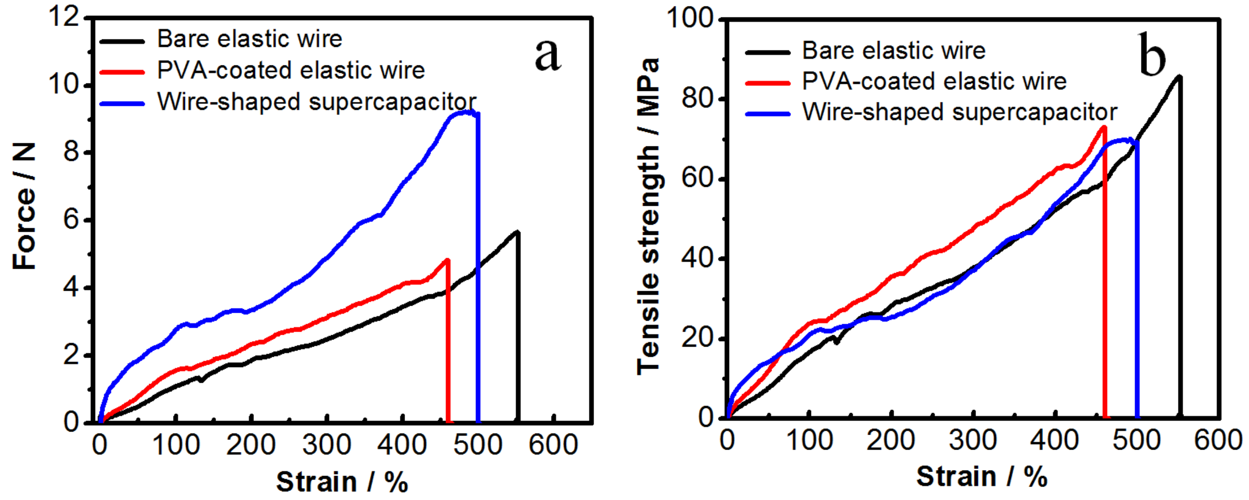

Figure S4. (a) Force-strain curves of elastic wires and assemble device. (b) Tensile strength-strain curves of elastic wires and devices.

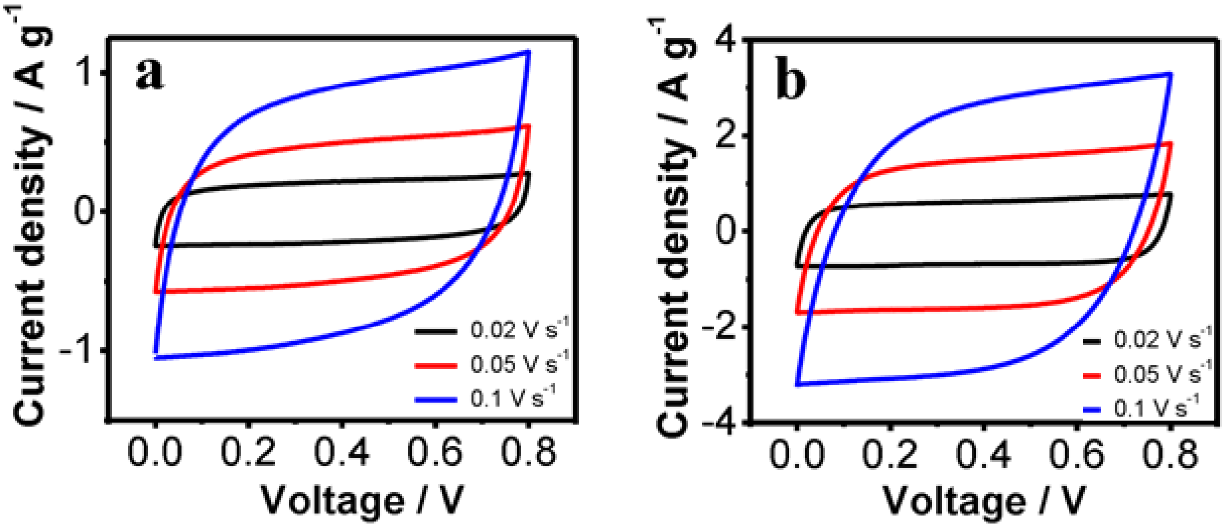

Figure S5. CV curves of the wire-shaped supercapacitor based on the bare CNT-wrapped (a) and CNT/PEDOT-PSS-wrapped (b) wire electrodes at different scanning rates.

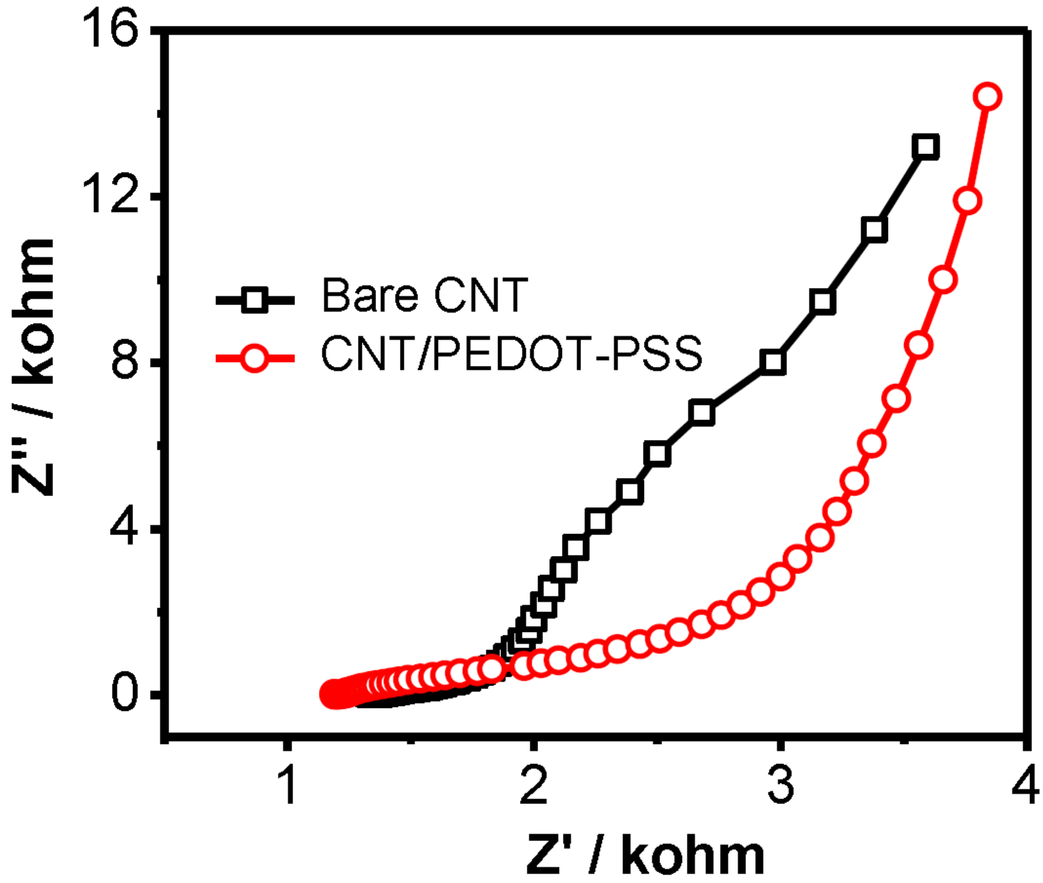

Figure S6. Nyquist plots of supercapacitors using the bare CNT-wrapped and CNT/PEDOT-PSS-wrapped elastic wire electrodes within a frequency range from 10^{-2} to 10^{5} Hz.

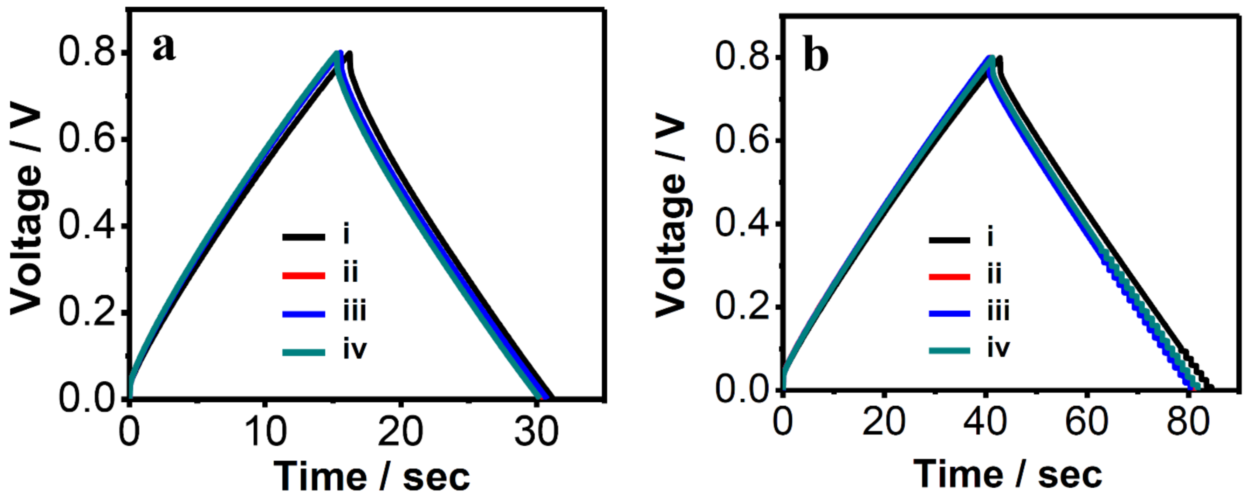

Figure S7. GCD curves of supercapacitor cells based on the bare CNT-wrapped (a) and CNT/PEDOT-PSS-wrapped (b) elastic wire electrodes under different bending states (*cf.* Figure 4a) at a constant current density of 0.5 A g^{-1}.

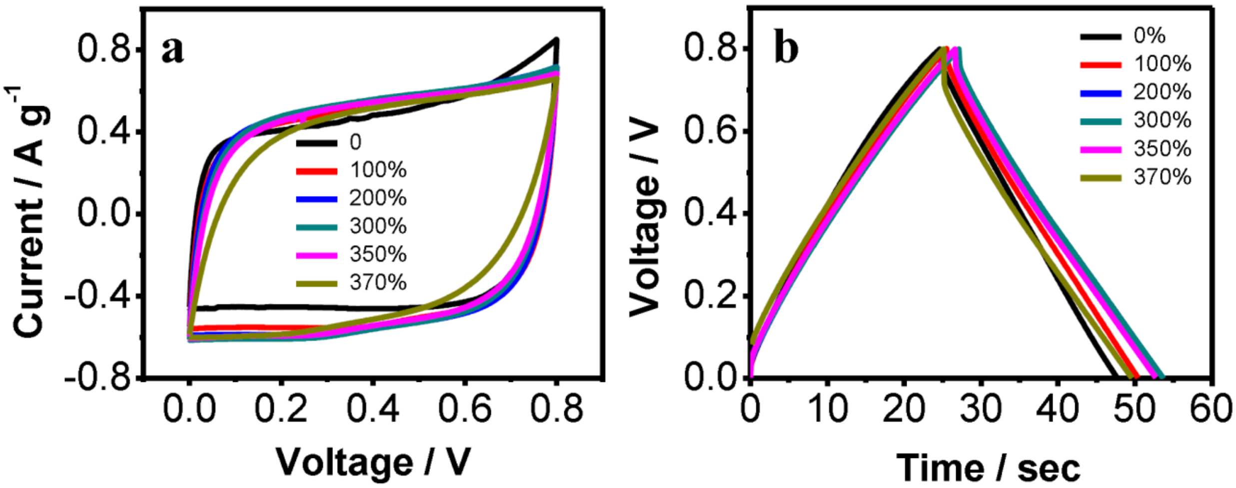

Figure S8. (a) CV curves of a wire-shaped supercapacitor cell based on the bare CNT-wrapped elastic wire electrodes under different stretching strains collected at a scanning rate of 0.05 V s^{-1}. (b) GCD curves of the wire-shaped supercapacitor cells under different stretching strains recorded at a constant current density of 0.33 A g^{-1}.

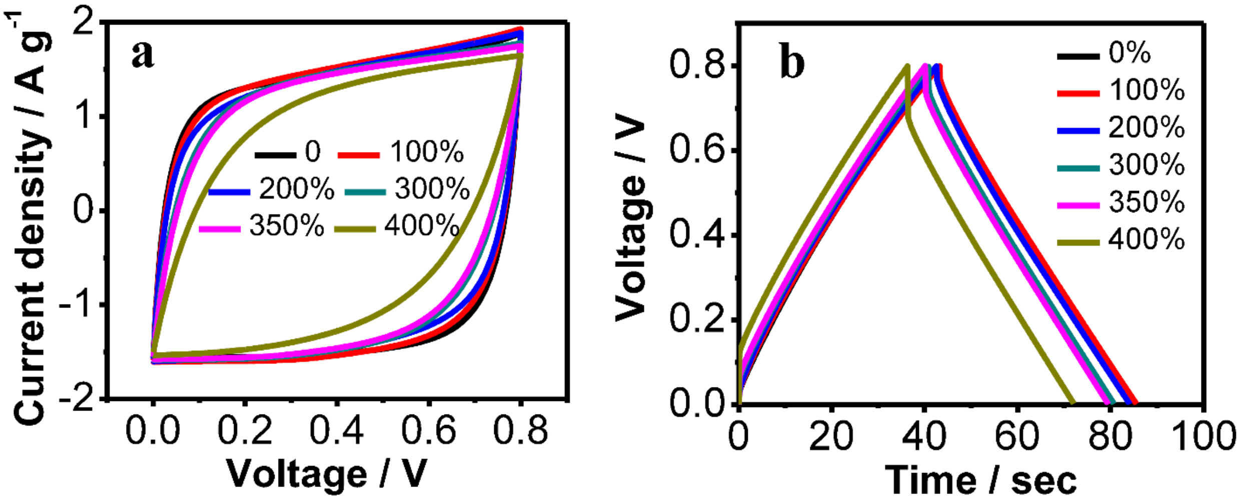

Figure S9. (a) CV curves of a wire-shaped supercapacitor cell based on the CNT/PEDOT-PSS-wrapped elastic wire electrode under different stretching strains collected at a scanning rate of 0.05 V s^{-1}. (b) GCD curves of the wire-shaped supercapacitor cells under different stretching strains recorded at a constant current density of 0.5 A g^{-1}.

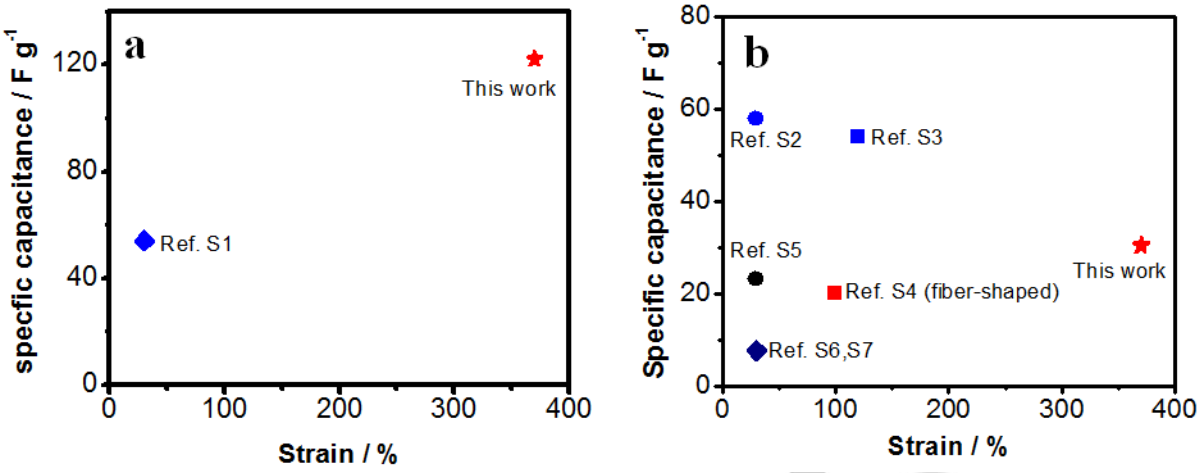

Figure S10. Comparison of (a) single electrode capacitance or (b) cell capacitance and stretchability of this work with other reported results. All the points apart from red colored ones are from film-type stretchable supercapacitors.

Table S1. Summary of the values of cell capacitance with respect to % strain for the device based on bare CNTs and CNT/PEDOT-PSS electrodes.

Sample \ Strain	0%	50%	100%	150%	200%	250%	300%	350%
CNT (F g^{-1})	8.0	8.2	8.3	8.4	8.6	9.0	8.9	8.7
CNT/PEDOT-PSS (F g^{-1})	30.7	31.4	31.9	31.9	31.9	30.9	30.7	29.9

References

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